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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Process for producing Silver Salt of Benzotriazole

We, FUJI SHASHIN FILM KABUSHIKI KAISHA, a Japanese Company of No. 210, Nakanuma, Minami Ashigara-Machi, Ashigara-Kamigun, Kanagawa, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the production of fine crystals of the silver salt of benzotriazole which are suitable for use in the manufacture of light-sensitive materials.

The grain size of silver salt particles contained in light-sensitive layers for photographic materials is important because it is generally considered that coarse silver particles are formed by the development of coarse silver salt particles, whereas fine silver salt particles are necessary for the development of fine silver particles. Since, moreover, as described for example in Mees, "The Theory of the Photographic Process"; page 814, published in 1954 by Macmillan, New York, it is generally believed that the diameter of the developed silver particles is directly proportional to its photometric constant, and the diameter of the developed silver particles is thus inversely proportional to its covering power. A high image density can therefore be obtained from a small amount of developed silver in the form of silver particles of small diameter.

According to the same reference, light-sensitive materials incorporating fine silver salt particles are also preferable for obtaining images having higher resolving power.

It is therefore desirable to use fine silver salt particles for preparing photographic light-sensitive materials. In conventional photographic silver halide light-sensitive materials, the size of silver halide particles is controlled by mixing a solution of an alkali metal halide and a solution of silver nitrate in the presence of a high molecular protective colloid such as gelatin or polyvinyl alcohol.

[*Price 4s. 6d.*]

Although organic silver salts can be used for preparing light-sensitive materials which are heat-developable without the need for fixing procedures, by preparing the salts in the form of coarse crystals which are thereafter pulverised, this procedure is time- and labour-consuming.

The present invention provides a process for the direct production of the silver salt of benzotriazole in a fine crystalline form, suitable for use in the manufacture of heat-developable light-sensitive materials capable of providing images having a high density and good resolving powder.

Accordingly, the present invention provides a process for the production of crystalline silver salt of benzotriazole, which comprises mixing together:

a solution of silver nitrate in a first solvent (A) which is a solvent for the silver nitrate and for nitric acid formed during the reaction of the silver nitrate and benzotriazole but which does not substantially dissolve the silver salt of benzotriazole formed, and

a solution of benzotriazole in a second solvent (B) which is a solvent for the benzotriazole and dissolves from 1 to 30% by weight of the total of the two solvents, of the first solvent, but which does not substantially dissolve the silver salt of benzotriazole formed, whereby crystals of the silver salt of benzotriazole are precipitated.

The solubility of the solvent A in solvent B is from 1 to 30% by weight of the total amount of the solution. If its solubility is too great, coarse crystals of the silver salt of benzotriazole will be formed. On the other hand, if the solubility of the silver salt solvent in the benzotriazole is too small, the yield of the silver salt of benzotriazole is poor. Suitable benzotriazole solvents (B) include for example phosphoric acid esters, phthalic acid esters, dibasic aliphatic acid esters of alcohols or phenols of glycerine esters of higher aliphatic acids. The silver nitrate solvent (A)

may be for example water, and the solvent (B) may then comprise, for example tricresyl phosphate (T.C.P.), dimethoxyethyl phthalate, di-*n*-butyl phthalate, diethyl sebacate, monooctyl-dibutyl phosphate, tri-*n*-butyl phosphate and castor oil. Where the solvent (A) is dimethyl formamide or dimethyl sulphoxide, then cotton seed oil, linseed oil, or camellia oil may be used as the solvent (B).

A volatile liquid is also preferably selected for washing the precipitated silver salt and which can mix with each of the two solvents in any desired ratio and which can make a three-component homogeneous phase containing more than about 10% of each solvent. The washing liquid should not, of course, dissolve substantial amounts of the benzotriazole silver salt. Examples of such a washing liquid include ethanol, methanol and acetone.

For selecting the solvents, including the washing liquid, for use in the invention, it is necessary not only to know the solubilities of the silver nitrate and benzotriazole reactants, as well as the products, e.g., nitric acid and the silver salt of benzotriazole, in each solvent, but also to know the mutual solubility curves of silver nitrate solvent A, benzotriazole solvent B and washing liquid C. Examples of these curves are shown on trigonometric coordinates, in the single figure of the accompanying drawing. The upper region above each curve stands for a composition wherein the three solvents form a homogeneous phase, while the region below the curve stands for a composition wherein they cause phase separation. The range XY on the base line is the limit of the mutual solubility of the silver and benzotriazole solvents, that is, the curves must cut the base line in this range, in order to obtain fine crystals of the silver salt of benzotriazole in accordance with the present invention.

The curves must also be lower than the point P. This ternary, homogeneous composition contains at least 10 %of each of the solvents in the washing liquid. Since washing liquid C can be mixed with solvent A in any desired ratio, the curves do not cross side AC but lead asymptotically to it.

The particular liquid systems presented in the drawings are given in Table 1.

TABLE 1

Curve	Solvent A	Solvent B	Washing liquid C
I	Water	Tricresyl phosphate	Methanol
II	Water	Tri-*n*-butyl phosphate	Acetone (temperature 25°C)

When the silver salt of benzotriazole is prepared, at normal temperature, by quickly mixing gram equivalents of silver nitrate and benzotriazole dissolved in equal quantities of the above solvents and washed with the appropriate washing liquid, it may be obtaintd as spindle-like crystals having a length of from 0.1 micron to 3 microns. The crystal particles are obtained in a liquid phase enriched with solvent B which separates out, whereas the nitric acid product is mainly present in a separate liquid phase eniched with solvent 9. In order to recover the fine crystals of benzotriazole silver, the liquid phase enriched with solvent A is removed by decantation or other method and the remaining phase, enriched with solvent B and containing silver salt of benzotriazole, is washed repeatedly first with solvent A or other solution, and then with washing liquid C. The residue is then dried to evaporate off washing liquid C and the silver salt of benzotriazole is obtained in the form of fine crystals.

In the conventional method for preparing the silver salt of benzotriazole, in which water is used as a solvent for silver nitrate and a solvent, e.g. methanol, which is completely miscible with water for benzotriazole, the grain size of the crystal of the thus formed silver salt of benzotriazole is large.

For example, silver salt of benzotriazole obtained by mixing the methanol and water solutions in the above conditions is in the form of spindle-like crystal particles or needle-like crystal particles having a length of from 10 microns to 100 microns and even after pulverising and dispersing these large crystal grains in a high molecular weight binder for preparing heat developable light-sensitive materials, when they are subjected to a mechanical treatment for a considerable period of time using a ball mill or a homogenizer, the size of the thus obtained crystal particle is at best about 10 microns, and the covering power of the developed silver image and the image density obtained, as well as the resolving power of such a light-sensitive material, are all low.

The fine crystals of the silver salt of benzotriazole obtained in accordance with the inven-

tion may be used for the preparation of heat-developable light-sensitive materials, and a dispersion of the fine crystal particles can be formed easily in a high molecular weight binder for this purpose. Further, the heat-developable light-sensitive material prepared using the silver salt of benzotriazole prepared according to the present invention can provide images having a high density and a good resolving power.

The conditions for mixing a silver nitrate solution and a benzotriazole solution in accordance with the invention are not limited to those above-mentioned, but the concentration of the solutions, the temperature of the solutions, the mixing rate, and the stirring conditions may be varied according to the particle size desired.

EXAMPLE 1

12 g. of benzotriazole at 50°C were dissolved in 100 ml. of tricresyl phosphate and the temperature of the resulting solution was adjusted to 35°C. 17 g. of silver nitrate were dissolved in 100 ml. of water and after adjusting the temperature thereof to 35°C, this solution was added quickly to the benzotriazole solution with stirring. After removing the aqueous phase which formed, the remaining liquid phase was washed with fresh water and after adding methanol thereto, the dispersion was washed while filtering. The crystals obtained were dried between dry filter papers; to give 16 g. of the silver salt of benzotriazole, of average grain size diameter 0.2 micron.

EXAMPLE 2

The procedure described in Example 1 was repeated using tributyl phosphate instead of tricresyl phosphate and methanol as the washing liquid. The average grain size of the 17 g. of silver benzotriazole particles obtained was 0.25 micron.

EXAMPLE 3

The procedure described in Example 1 was repeated by using di-n-butyl phthalate as the solvent for benzotriazole, dimethyl formamide as the solvent for silver nitrate, and acetone as the washing agent. The average particle size of the crystals obtained was 1.0 micron.

EXAMPLE 4

The procedure described in Example 1 was repeated by using di-n-butyl phthalate as the solvent for benzotriazole, dimethyl sulphoxide as the solvent for silver nitrate, and methanol as the washing liquid. The average particle size of the crystals obtained was 1.0 micron.

EXAMPLE 5

The procedure described in Example 1 was repeated by using castor oil as the solvent for benzotriazole and dimethyl formamide as the solvent for silver nitrate. The temperature at mixing was 60°C. Ethanol was used as the washing liquid. The average particle size of the crystals thus obtained was 0.6 micron.

EXAMPLE 6

Light-sensitive compositions having the following components were applied to photographic papers, using (a) coarse particles (of size 10 microns) of the silver salt of benzotriazole prepared from a water-methanol solvent system as a control and (b) the fine crystals (size 0.2 and 0.25 microns) of the silver salts of benzotriazole prepared by the procedures in Examples 1 and 2. Ethanol was used as the solvent for coating:

Polyvinyl butyral	6.0 g.
Silver salt of benzotriazole	1.2 g.
Strontium iodide ($6H_2O$)	0.055 g.
Sensitising dye	0.0001 g.
Hydroquinone	0.3 g.
Sebacic acid	4.0 g.

After exposure to illumination from a tungsten lamp, the papers were heated for 10 seconds to 140°C. to provide images. The maximum image densities and the resolving powers are compared in Table 2, which shows that the silver salt of benzotriazole prepared by the process of the present invention gave improved results.

TABLE 2

	Silver salt source		
	Control	Example 1	Example 2
Max. density	1.0	1.3	1.6
Resolving power line/mm.	2.5	3.2	4.0

EXAMPLE 7

The procedure of Example 6 was repeated except that 0.3 g. of 4-methoxy-1-naphthol was used instead of hydroquinone in the light-sensitive composition and the light-sensitive papers prepared were heated, after exposure, for 10 seconds to 120°C. The image densities and the resolving powers are shown in Table 3, from which it is confirmed that the silver salt of benzotriazole prepared by the process of this invention gives improved results.

TABLE 3

	Silver salt source		
	Control	Example 1	Example 2
Max. density	1.0	2.1	1.5
Resolving power line/mm.	3.2	5.0	4.0

WHAT WE CLAIM IS:—

1. A process for the production of crystalline silver salt of benzotriazole, which comprises mixing together:

a solution of silver nitrate in a first solvent which is a solvent for the silver nitrate and for nitric acid formed during the reaction of the silver nitrate and benzotriazole but which does not substantially dissolve the silver salt of benzotriazole formed, and

a solution of benzotriazole in a second solvent which is a solvent for the benzotriazole and dissolves from 1 to 30% by weight of the total of the two solvents, of the first solvent, but which does not substantially dissolve the silver salt of benzotriazole formed, whereby crystals of the silver salt of benzotriazole are precipitated.

2. A process according to Claim 1 wherein the first solvent comprises water, dimethyl formamide or dimethyl sulphoxide.

3. A process according to Claim 1 or 2 wherein the second solvent comprises tricresyl phosphate, tri-*n*-butyl phosphate, dimethoxyethyl phthalate, di-*n*-butyl phthalate, diethyl sebacate or castor oil.

4. A process according to Claim 2 wherein the silver salt solvent comprises dimethyl formamide or dimethyl sulphoxide and the benzotriazole solvent comprises cottonseed oil, linseed oil or camellia oil.

5. A process according to any of the preceding Claims, which includes the step of washing the precipitated silver salt with a volatile liquid in which each of the said solvents is completely miscible in all proportions and with which both the said solvents form a homogeneous ternary mixture containing more than 10% by weight of each of the said solvents.

6. A process according to Claim 5, wherein the washing liquid comprises methanol, ethanol or acetone.

7. A process for the production of crystals of the silver salt of benzotriazole as claimed in Claim 1, substantially as described with reference to any of the accompanying Examples.

8. The silver salt of benzotriazole whenever prepared by the process claimed in any of the preceding Claims.

9. The silver salt of benzotriazole as claimed in Claim 8, in the form of spindle-like crystals having a length of 0.1 to 3 microns.

10. Light-sensitive material comprising the silver salt of benzotriazole claimed in Claim 8 or 9 incorporated in a polymeric support medium.

11. Heat-developable photographic paper bearing silver benzotriazole as claimed in Claim 8 or 9, substantially as described with reference to Example 6 or 7.

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1 SHEET

COMPLETE SPECIFICATION

This drawing is a reproduction of the Original on a reduced scale.